STANFORD UNIVERSITY LIBRARY
APR 13 1927

THE CATALYTIC EFFECT OF BUFFER SOLUTIONS

BY

MILTON BERGSTEIN, Sc.M.

L.C

THIS THESIS

HAS BEEN ACCEPTED BY THE GRADUATE SCHOOL OF NEW YORK UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

JUNE 1925

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

3781
N53B
Unclassed
Dissertation

THE CATALYTIC EFFECT OF BUFFER SOLUTIONS

BY

MILTON BERGSTEIN, Sc.M.

THIS THESIS

HAS BEEN ACCEPTED BY THE GRADUATE SCHOOL OF NEW YORK UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

JUNE 1925

THE CATALYTIC MINIMUM POINT[1]

BY M. BERGSTEIN[2]

On the basis of the protion theory of chemical reactivity Rice[3] has predicted that for those reactions catalyzed both by hydrogen and hydroxyl ions in aqueous solutions the point of minimum catalytic activity (maximum stability of the compound) will be practically the same for all reactions and will be on the acid side. In support of this view the work of Karlsson[4] on ethyl and methyl acetates was cited. Karlson working at 85.55° C. found a minimum for methyl acetate at pH 4.70 and for ethyl acetate at pH 5.10. From the work of Dawson and Powis[5] on the autocatalytic reaction between acetone and iodine Rice calculates a minimum at pH 4.7.

More recently Bolin[6] has reported the following points of maximum stability.

TABLE I

T °C.		pH
20	Ethyl ester of formic acid	4.65
20	" " " monochloracetic	4.8
20	" " " aminoacetic	3.8
80	Benzamid	5.8
40	Acetanilid	6.2

On the basis of these results Bolin criticises the unhydrated ion theory as applied to hydrolysis. He states that the results for benzamid are not at all in harmony with the theory of Rice. In order to apply the theory one must assume either that the benzamid affects the hydration of the hydrogen and hydroxyl ions differently or that the dissociation constant of water is changed by the benzamid. In view of the small solubility of the benzamid and the pH values these appear improbable.

Karlsson[7] in a more recent study has repeated his work with ethyl and methyl acetates at lower temperatures and extended the experiments to other esters. He endorses the hypothesis of Euler[8] that the esters may be regarded as amphoteric substances.

---

[1] Contribution from the Havemeyer Chemical Laboratory of New York University and the Chemical Laboratory of Johns Hopkins University. Constructed in part from a thesis presented by M. Bergstein in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Graduate School of New York University, June 1925.

[2] University Fellow, New York University, 1924-25.

[3] Rice: J. Am. Chem. Soc., **45**, 2808 (1923).

[4] Karlsson: Z. anorg. Chem., **119**, 69 (1921).

[5] Dawson and Powis: J. Chem. Soc., **101**, 1502 (1912).

[6] Bolin: Z. anorg. Chem. **143**, 201 (1925).

[7] Karlsson: Z. anorg. Chem., **145**, 1 (1925).

[8] Euler and Laurin: Sr. Vet. Akad. Arkiv für Kemi, **7**, 30 (1920).

In his earlier work Karlsson reported a distinct shift of the minimum point toward the acid side upon the addition of salts. His later results do not show an appreciable displacement of the minimum point. He attributes the discrepancies to experimental errors in the earlier work. Karlsson's experiments were carried out in buffer solutions. The effect of change of the total equivalent salt concentration on the reaction rate in buffer solutions has been discussed in several recent papers.[1] From the protion theory as presented by Rice we would expect the addition of salts to shift the minimum point to the acid side. In addition the effect of temperature would be to shift the minimum point toward the alkaline side. These considerations would not apply in buffer solution but should apply to the autocatalytic reaction between acetone and iodine in aqueous solution. This reaction has been the subject of a number of studies in acid solution. The reaction in acid solution may be represented by the stochiometric equation

$$CH_3COCH_3 + I_2 + H^+ \longrightarrow CH_3COCH_2I + H^+ + I^-$$

Since the rate of the reaction is independent of the concentration of I_2, Dawson and Powis gave as the equation expressing the velocity

$$dx/dt = k(a-x)(c + x)$$

where x is the amount of iodine which has disappeared at time t, a is the initial concentration of acetone, and c is the initial hydrogen ion concentration. In the actual experiments the solution was .1 M in acetone and .005 M in iodine, x being negligible in comparison with a. They wrote therefore,

$$dx/dt = k\ a(c + x),$$

and integrating, they obtained

$$\ln \frac{c + x}{c} = kat.$$

Extrapolating to zero time they found c to be equal to 2.1×10^{-5} (the mean of three observations). When a small quantity of hydrochloric acid was added to the solution and this concentration of hydrogen ion 2×10^{-5} N subtracted from the initial value obtained by extrapolation, c was found to equal 1.4×10^{-5}. They concluded that the catalytic substance whose activity was represented by this initial hydrogen ion concentration was actually alkaline in nature. When sodium hydroxide was added to the reaction mixture extrapolation yielded a value for c of 2×10^{-5}. On the whole they could present no satisfactory theory to explain the anomalous catalytic activity of pure water.

Their trouble lay in the fact that they neglected the not inappreciable catalytic activity of the hydroxyl ions in pure water. One of us (M. B.) has shown, in an unpublished research, that the rate of the reaction at pH 7 is approximately twice that at pH 2. As has been indicated above, neutral water is catalytically active. Therefore, the iodine-acetone reaction starting in a neutral solution will proceed at a rapid rate, liberating H^+ ion and removing OH^- ion until a point is reached where the products of the concentra-

[1] Brönsted and Teeter: J. Phys. Chem., **28**, 579 (1924); Brönsted and King: J. Am. Chem. Soc., **47**, 2523 (1925); Kilpatrick: **48**, 2091 (1926).

tions of each of them by their catalytic activities are equal. This condition is reached practically instantaneously and cannot be measured because only a minute quantity of iodine has disappeared. At this point the reaction has minimum velocity and gradually accelerates because of the liberation of hydrogen ion. We may consider this point to be the initial point of the reaction. It is actually the catalytic minimum point.

Dawson and Powis's reaction velocity equation is subject to the criticism that it does not recognize the existence of two interdependent catalytic substances at the initial point. If we ascribe half of the effect that they observed to hydrogen ion, we may assume that catalytically neutral water as a hydrogen ion concentration of 10^{-5}, but this statement is, as the following analysis discloses, far from exact.

Consider the reaction

$$CH_3COCH_3 + I_2 + H^+ + OH^- \longrightarrow CH_3COCH_2I + I^- + 2H^+ + OH^-$$

Let

a = initial concentration of acetone,
c = initial concentration of hydrogen ion,
d = concentration of hydroxyl ion at time t,
x = mols of I_2 reacted at time t.
k_H = catalytic activity of hydrogen ion.
k_{OH} = catalytic activity of hydroxyl ion.

Then $dx/dt = (a - x)\,[k_H(c + x) + k_{OH}\,d]$. It is known that $(c + x)\,d = 10^{-14}$ and we may therefore write $d = 10^{-14}/(c + x)$. The constants k_H and k_{OH} are also related. We shall not consider the secondary effect: the formation of iodoform which is also catalyzed by hydroxyl ion in alkaline solution. In catalytically neutral water the rate of reaction due to hydrogen ion is equal to the rate due to hydroxyl ion or

$$k_H c = k_{OH}\,10^{-14}/c$$

or

$$k_{OH} = c^2/10^{-14}k_H$$

The equation then takes the form

$$\frac{dx}{dt} = k(a-x)\,\left(c + x + \frac{c^2}{c + x}\right)$$

where $k = k_H$. The solution of this equation is

$$kt = \frac{a + c}{(a + c)^2 + c^2} \ln \frac{\sqrt{(c + x)^2 + c^2}}{a - x} - \frac{c}{(a + c)^2 + c^2} \tan^{-1} \frac{c + x}{c} + K$$

On removing negligible quantities the above equation yields

$$kt = \frac{1}{a} \ln \frac{\sqrt{(c + x)^2 + c^2}}{a - x} + K$$

When $t = 0$, $x = 0$. Therefore, $K = -\frac{1}{a} \ln \frac{c\sqrt{2}}{a}$, and

$$k = \frac{1}{at}\left(\ln \frac{\sqrt{(c + x)^2 + c^2}}{a - x} - \ln \frac{c\sqrt{2}}{a}\right)$$

If the initial molar concentration of acetone is about twenty times that of iodine (as is true in the experiments reported), x is negligible in comparison with a and the equation may be simplified to

$$k = \frac{1}{at} \ln \sqrt{\frac{(c + x)^2 + c^2}{2\,c^2}}$$

In order to make a determination of c the following device is resorted to. For large values of t (and therefore of x), c^2 and 2 cx are negligible in comparison with x^2. We may write in this case

$$k\,at + \ln c\sqrt{2} = \ln x$$

It is now possible to determine c without knowing either k or a. Plotting ln x as ordinate against t as abscissa the intercept is equal to ln $c\sqrt{2}$. Thus c may be determined. The experimental details follow.

Solutions were made up containing .2% potassium iodide and approximately .005 M iodine. To this was added a known weight of acetone from a calibrated pipette, the flask was filled to the mark with distilled water and shaken, and the time was noted as zero time for reactions conducted at 25°. Two samples were removed with a calibrated pipette and titrated against standard sodium thiosulphate using a weight burette. The remainder of the solution was transferred through a quick running siphon to glass-stoppered 80 cc. bottles and the bottles were placed in the thermostat. When the experiments were conducted at temperatures of 30° and above, a time 12 minutes after the bottles were placed in the thermostat was noted as zero time. Two 25 cc. samples were taken from each bottle at regular intervals and the iodine concentrations were determined by titration against sodium thiosulphate. The reactions were stopped by running the solutions into a mixture of acetate buffer of approximately pH 5 and a known weight of thiosulfate. Starch solution was added and the solution titrated to the disappearance of the blue with sodium thiosulphate form a weight burette. When the experiments were run at 25° and 30° the time noted as final for each sample was the time at which the reaction mixture started to run from the pipette into the titrating flask. At higher temperatures the reactions were stoppered by placing the reaction vessels in a freezing mixture. The final time noted in such cases was taken as two minutes after the bottles were placed in the freezing mixture. Check runs were made without any acetone using only the iodine solution and the error due to volatilization of iodine from the glass-stoppered reaction vessels was found to be negligible. Because, as previously stated the hydrogen ion concentration of the water almost immediately came to approximately 10^{-5}, conductivity water was not required, ordinary distilled water being satisfactory, and any alkalinity due to potassium iodide could be neglected.

The value for the catalytic minimum point in the above experiment was obtained as follows. The drop in titre of the solution in terms of grams of $Na_2S_2O_3$ solution per 24.92 cc. of sample taken was plotted along the logarithmic axis on semi-logarithmic paper against the time plotted along the ordi-

TABLE II

The Autocatalytic Iodine-Acetone Reaction at 25°

2 L of soln. containing 27.54 g. acetone; 2% KI

.005344 M $Na_2S_2O_3$ 24.92 cc. sample

Time (hours)	Titre	Time	Titre
0	24.66	192.7	12.25
26.5	24.53	196.8	11.29
73.6	24.16	197.4	10.70
119.9	22.77	216.1	3.10
142.1	21.42	220.7	1.25
165.9	18.69		

Catalytic minimum point $[H^+]$ 1.57×10^{-5}; P_H 4.81

nary axis. The points plotted, with the exception of the earlier ones, lay on a straight line which, of course, intersected the logarithmic axis at zero time. The point of intersection represented the apparent drop in titre per 24.92 cc. at zero time. Multiplying this value by the molarity of the sodium thiosulfate and dividing by the volume of the sample taken gives the apparent initial hydrogen ion concentration which is $c\sqrt{2}$. For experiment 103

$$c\sqrt{2} = \frac{.106 \times .005344}{24.92} = 2.274 \times 10^{-5}$$

$$c = 1.57 \times 10^{-5}$$

Table III summarizes a series of experiments carried out in the same manner. In the experiments at 40° C. and 45° C. the concentration of the acetone was .137 M, in the others .237 M. 0.2% KI was present in all experiments.

TABLE III

Temperature °C.	Minimum point $[H^+] \times 10^{-5}$	P_H
25	1.57	4.81
25	1.30	4.88
25	1.66	4.79
30	1.57	4.81
30	1.49	4.82
35	1.62	4.80
35	1.57	4.81
35	1.42	4.84
40	1.65	4.79
40	1.56	4.81
45	1.79	4.74
45	1.74	4.75

From Table III it is evident that any variation in the minimum point with temperature is within the experimental error of the measurements. From data on ester hydrolysis the minimum point can be calculated at 20° C. to

be at P_H 5.47 and at 40° C. at P_H 5.35. The mean value determined for the catalytic minimum point in the above experiments ranging from 25° C. to 45° C., is $[H^+] = 1.58 \times 10^{-5}$ or pH 4.8.

Table IV summarizes the results in the presence of neutral salts. All experiments were carried out at 35° C.

TABLE IV

Salt added Molarity	Minimum point $[H^+] \times 10^{-5}$	P_H
0	1.62	4.80
0	1.57	4.81
.616 KCl	1.88	4.72
1.267 KCl	1.94	4.72
.830 NaCl	1.46	4.85
1.635 NaCl	1.36	4.87

It is apparent that if there is any neutral salt effect it is within the experimental error of the measurements.

Other Catalytic Minimum Points

Wijs[1] studying the saponification of methyl acetate in water found a minimum at pH 5.42 at 24.8° C.

Euler and Laurin found pH 5.10 for ethyl acetate at 69.3° C. Hudson[2] studying the mutarotation of glucose, using the data of Osaka[3] and his own calculated the minimum to be at pH 4.64 at 24.7° C. More recently Euler[4] reports the point of minimum catalytic activity for the same reaction at pH 5.0 for 5.2° C.

Bogue[5] in discussing the hydrolysis of collagen noted that the region from pH 4.5 to 6.0 should be avoided as the hydrolysis is very slow at that concentration of hydrogen ions.

The relation of the minimum point to the isoelectric points of proteins has been discussed by Thomas and Kelly.[6]

Many other examples of phenomena which involve consideration of a minimum point in the neighborhood of pH 5 may be found in the fields of industrial and biological chemistry.

One of us (M. B.) wishes to express his thanks to Dr. F. O. Rice of Johns Hopkins University for directing his work in this investigation.

[1] Wijs, Z. physik. Chem., **11**, 492 (1893).
[2] Hudson: J. Am. Chem. Soc., **29**, 1571 (1907); **31**, 1136 (1909).
[3] Osaka, Z. physik. Chem., **35**, 702 (1900).
[4] Euler: Z. anorg. Chem., **146**, 45 (1925).
[5] Bogue: J. Ind. Eng. Chem., **15**, 1154 (1923).
[6] Thomas and Kelly: J. Ind. Eng. Chem., **15**, 1148 (1923).

Summary

1. The catalytic minimum point for the reaction between iodine and acetone has been found to be at pH 4.8.

2. This value is unaffected within the limits of experimental error by either temperature or neutral salts.

3. The results do not support the unhydrated ion theory of catalysis as proposed by Rice.

New York, N. Y.
Baltimore, Md.